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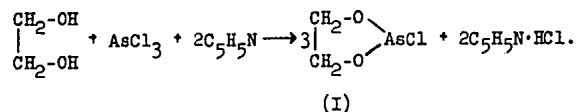
## THE ESTERS OF E'HYLENEGLYCOLARSENOUS ACID

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/The experimental part of this article has been omitted./

Detailed investigations of cyclic derivatives of arsenous acid were started in our laboratory in 1950 [1, 2]. No one had studied the cyclic esters of ethyleneglycolarsenous acid until then. In the present report, we will describe data we obtained by studying the acid chloride and the mixed esters of ethyleneglycolarsenous acid containing a five-membered ring.

By reacting an equimolecular quantity of arsenic trichloride with ethylene glycol in absolute ether in the presence of anhydrous pyridine, we synthesized the cyclic acid chloride of ethyleneglycolarsenous acid (I) as the main product of the reaction according to the following equation:



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## CLASSIFICATION

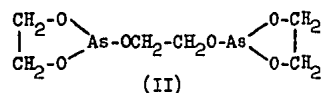
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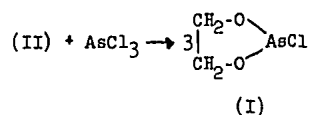
We also clarified the fact that in this reaction the complete ethyleneglycol ester of arsenous acid (II) is formed as well as the acid chloride (I):



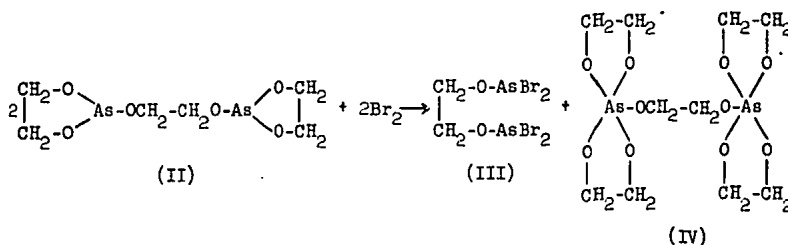
The experiment on the interaction of the acid chloride of ethyleneglycolarsenous acid with ethylene glycol in the presence of pyridine in absolute ether led to an analogous end result. In this manner, it was established that ester (II) is formed as a result of the secondary reaction.

The complete ethyleneglycol ester of arsenous acid (II) can also be obtained in a very good yield of about 89-92% by the direct action of arsenous acid anhydride on ethylene glycol at a temperature of 140-150°. This reaction is reversible; with an excess of water, the ester is completely hydrolyzed to form arsenous acid anhydride and ethylene glycol.

When an equimolecular quantity of arsenic trichloride acts on (II), the acid chloride of ethyleneglycolarsenous acid (I) is formed in an almost quantitative yield according to the equation:



The ethyleneglycol ester of arsenous acid (II) does not react with methyl iodide even with heating, nor does it add sulfur or cuprous bromide. The reaction of its bromination takes place in a very unique manner. Instead of the expected addition of two bromine molecules, only half of the calculated amount, i.e., exactly one bromine molecule is added in the reaction. In this reaction, a very interesting conversion takes place with a complicated rearrangement of radicals. We formerly gave the following scheme for the course of the reaction [1]:



The formation of the acid bromide (III) under the conditions of the experiment has been confirmed experimentally. The acid bromide is a green liquid having a mustard-like odor and a boiling point of 86° at 11 mm.

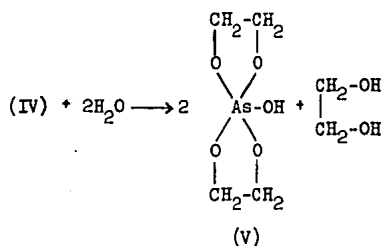
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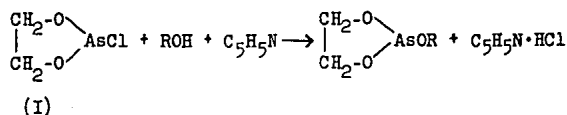
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The second compound of pentavalent arsenic which we isolated (lustrous crystals with a melting point of  $127^{\circ}$ ) is very soluble in many organic solvents and in water. It does not hydrolyze in the cold. The aqueous solution has an acidic reaction and can be titrated with 0.1 N NaOH. The hypothetical structure [1] which we ascribed previously to compound (IV) is doubtful. Further investigation revealed that this compound is diethyleneglycolarsenic acid (V), described by Englund [3]. However, in contrast to Englund's preparation, ours had a melting point of  $127^{\circ}$  instead of  $120^{\circ}$ ; the molecular weight, determined according to Rast, is not double, although in a bromoform solution it is indeed close to double.

The formation of diethyleneglycolarsenic acid probably takes place by hydrolysis of the above-mentioned hypothetical compound (IV):

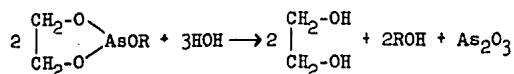


By treating the acid chloride of ethyleneglycolarsenous acid (I) with the corresponding absolute alcohols in the presence of pyridine in ethyl ether, we synthesized various mixed esters of ethyleneglycolarsenous acid according to the following scheme:



In this way, the following esters of ethyleneglycolarsenous acid were prepared and isolated: methyl, ethyl, n-propyl, n-butyl, n-hexyl, n-heptyl, n-octyl, nonyl, phenyl, and cyclohexyl.

The above-mentioned esters decompose comparatively easily as a result of the action of water, evolving heat and forming the corresponding alcohol, ethylene glycol, and arsenous acid anhydride.



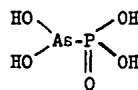
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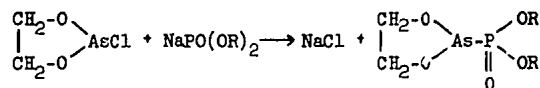
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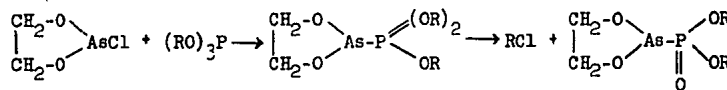
In an effort to obtain derivatives of the hypothetical acid:



we made unsuccessful attempts to carry out the following reactions:



and

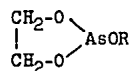
Conclusions

1. It was established that by the reaction between ethylene glycol and arsenic trichloride in absolute ether and in the presence of pyridine, it is possible to prepare the acid chloride of ethyleneglycolarsenous acid and the complete ethyleneglycol ester of arsenous acid.

2. A simpler and more convenient method was worked out for preparing the ethyleneglycol ester of arsenous acid by means of the reaction between ethylene glycol and arsenous acid anhydride.

3. The reaction of brominating the ethyleneglycol ester of arsenous acid has been investigated. The acid bromide having the composition  $[-\text{CH}_2\text{OAsBr}_2]$  and diethyleneglycolarsenous acid were isolated from the products of the reaction.

4. Cyclic-mixed esters having the composition:



were synthesized and their properties and reactions described.

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